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CITATION:

Hashida, Masaki ...[et al]. Crystal structures on a copper thin film with a surface of periodic self-organized nanostructures induced by femtosecond laser pulses. Physical Review B 2011, 83(23): 235413.

ISSUE DATE:

2011-06

URL:

<http://hdl.handle.net/2433/145964>

RIGHT:

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Crystal structures on a copper thin film with a surface of periodic self-organized nanostructures induced by femtosecond laser pulses

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(Received 2 March 2011; revised manuscript received 27 April 2011; published 13 June 2011)

Crystal structures on a single-crystalline copper film with a periodic self-organized surface induced by femtosecond laser pulses with fluences of 0.08–0.64 J/cm² have been analyzed by transmission electron microscopy. It was found that the crystal structures depend on laser fluence: polycrystalline structures are formed at fluences less than 0.2 J/cm², an amorphous state forms around 0.3 J/cm², and polycrystalline structures form again at fluences greater than 0.35 J/cm². The energy spectrum of ions emitted during the formation of periodic structures on the surface shows that the energy of copper ions is high enough to transform the crystal to an amorphous state. A conceptual mechanism for crystal structure transformation by the penetration of energetic ions generated in the process of self-organization of periodic structures is proposed.

DOI: [10.1103/PhysRevB.83.235413](https://doi.org/10.1103/PhysRevB.83.235413)

PACS number(s): 79.70.+q, 79.20.Eb, 78.20.Jq

I. INTRODUCTION

The crystal structures of a metal surface ablated by femtosecond laser pulses have been investigated by several groups using x-ray diffraction.^{1–4} The reduction of x-ray diffraction peaks showed partial formation of one-component amorphous metal at the thin surface layer for Au, Cu, Ag, and Fe. Even though the formation of one-component amorphous metal has not been forbidden theoretically^{5,6} for Au, Cu, and Ag, it could not be produced by conventional methods, such as rapid cooling with low-temperature rolling, evaporation with sputtering, and electroplating. The formation of amorphous metal is a key issue for the mechanism of femtosecond laser ablation, which has been analyzed by molecular dynamics (MD) simulations based on thermal diffusion. However, the thermal diffusion length (or heat-affected zone) calculated by MD simulation was much smaller than the experimental results. Therefore, some other process is needed to account for the formation of the amorphous state.

Recently, the formation of grating structures on metal surfaces has been observed.^{7–29} For fluence levels near the low-ablation threshold, the grating structures had interspaces of 300 nm, which was much shorter than the laser wavelength of 800 nm. The formation of grating interspaces, especially for Cu with a 100-fs laser pulse, depends on the fluence,³⁰ and this phenomenon is well explained by the parametric decay model³¹ proposed by Sakabe *et al.* We measured the dependence on laser fluence of the interspaces in Ti, Pt, Mo, and W (Ref. 7) and found that the experimental results agreed reasonably well with this model.

In a parametric decay model, a femtosecond laser pulse interacts with the metal and a photon in the IR region, creating a plasma wave that decays along the surface. The plasma wave produces an ion-enriched local area on the surface. These ions experience a strong Coulomb repulsive force and can be ejected into a vacuum: a Coulomb explosion³² occurs. Through this process, periodic grating structures are formed. This mechanism may also be responsible for the creation of amorphous metals. However, the relation between the formation of a surface grating structure and its crystallization has not been investigated because precise measurements of the

degree of crystallinity of the thin surface layer have not been conducted.

In this study, precise measurements of the degree of crystallinity of a copper thin film were carried out using a transmission electron microscope. The electron diffraction patterns in the laser fluence where the grating structure was formed were analyzed. To investigate the dynamics of amorphous metal formation, we considered a model in which energetic ions penetrate into the thin metal surface. The relation between the dynamics of ion emission through Coulomb explosion and the formation of amorphous metal is discussed.

II. EXPERIMENTS

The target material was copper of 99.9% purity coated on a sodium chloride crystal (100) substrate by conventional resistive evaporation techniques. To fabricate single crystals, the substrate was heated to 600 K and copper was deposited at a rate of a few angstroms per second. The size of the target was 3 × 3 mm², and its thickness was 200 ± 20 nm. The film was floating on distilled water and was caught on a metal grid (300# mesh). The copper thin film initially had a single-crystal structure (100), which was confirmed by transmission electron microscopy.

In the laser ablation experiments, a Gaussian transverse-mode laser beam (800-nm wavelength, 160-fs pulse duration, 10-Hz repetition rate) generated by a T⁶ laser system³³ was used. The laser beam was focused to a spot size of $\phi 40 \mu\text{m}$ on the target surface with a lens ($f = 30 \text{ cm}$) at an incident angle of 0° with respect to the target normal. The laser energy was varied by an energy attenuator from 0.5 to 10 μJ (corresponding to energy fluences in the range 0.04–0.8 J/cm²). The number of laser pulses irradiating the target surface for ablation was controlled by a mechanical shutter. Copper films with thickness of 30 nm were obtained by controlling the number of laser pulses. In the fluence range 0.20–0.76 J/cm², the number of laser pulses (from 1000 to a single pulse) was chosen using a mechanical shutter. The number of laser pulses was not varied at each laser fluence except at high laser fluence. At 0.2 J/cm², the ablation rate was

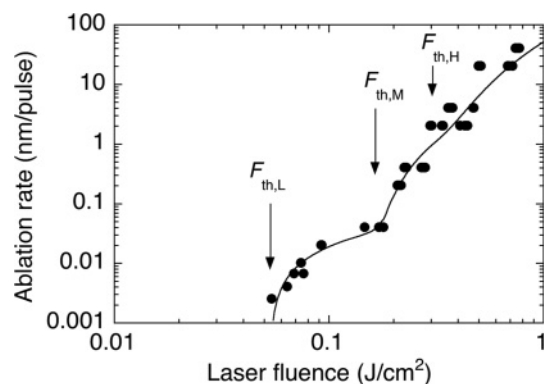


FIG. 1. Ablation dependence on laser fluence for Cu thin films irradiated with 160-fs laser pulses. A Cu film evaporated onto a NaCl substrate is used as a target. The thickness of the Cu thin films was 200 nm. Two ablation thresholds were identified at fluences of $F_{th,L} = 0.053 \text{ J/cm}^2$ and $F_{th,M} = 0.165 \text{ J/cm}^2$. The ablation rate dependence for Cu thin films is well explained by the model for Cu bulk metal, shown as a solid line. The model indicates that there is another ablation threshold at $F_{th,H} = 0.30 \text{ J/cm}^2$.

$\sim 0.17 \text{ nm/pulse}$. Thus, 1000 laser pulses were irradiated to obtain a 30-nm film from a copper film with an initial thickness of 200 nm. On the other hand, at the laser fluence of 0.77 J/cm^2 , the ablation rate was $\sim 43 \text{ nm/pulse}$ with large dispersion and unstable with pulse-to-pulse variation. Thus, one to four pulses were chosen to obtain the $\sim 30\text{-nm}$ film. The 30-nm film is suitable for electron diffraction measurement because the number of transmitted electrons decreases drastically with increasing thickness of the copper film. Additionally, if the film were thicker, the precision of measuring the degree of crystallinity of the copper thin film would be worse, because the ratio of the affected layer thickness to the unaffected layer thickness would be lower. For these reasons, the 30-nm film was chosen.

All the ablation experiments were performed in air at room temperature. The laser-ablated copper surface was observed with an optical microscope, an electron microscope (JEOL JSM-5560), and an atomic force microscope (Keyence VN-8000). The crystal structure of the copper thin films was measured on a transmission electron microscope (JEOL JEM-2000FX).

III. RESULTS AND DISCUSSION

Measurements of ablation rate were made in the fluence range $0.04\text{--}0.8 \text{ J/cm}^2$. Figure 1 shows the ablation rate dependence on laser energy fluence. The experimental results for Cu indicate the presence of three different ablation regimes. The lowest laser fluence $F_{th,L}$ was 0.053 J/cm^2 . At 0.165 J/cm^2 , the ablation rate increased sharply and the rate then showed a different dependence on laser fluence. Therefore, two ablation thresholds were identified at fluences of $F_{th,L} = 0.053 \text{ J/cm}^2$ and $F_{th,M} = 0.165 \text{ J/cm}^2$. The ablation thresholds obtained through the present experiment were of the same order of magnitude as the thresholds deduced by crater depth measurements reported previously.³⁴ The ablation rate dependence for Cu thin films is well explained by the model for Cu bulk metal (shown as a solid line in Fig. 1).

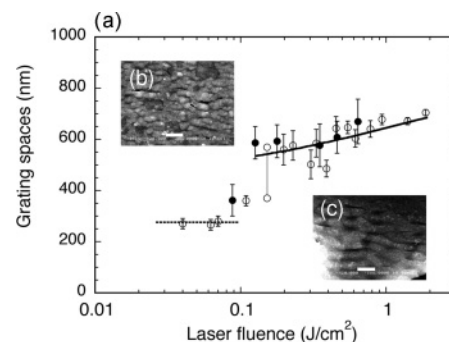


FIG. 2. (a) Laser fluence dependence of the interspaces of the periodic structures produced on copper by femtosecond laser pulses. The interspaces of copper thin film (solid circles) observed in the present experiment were in good agreement with the interspaces (open circles) of copper bulk metal reported in a previous study.³⁰ The solid line shows the result calculated according to the parametric decay model³¹ and the dotted line shows the calculation for a surface plasma wave directly induced by a laser. Surface morphologies of thin Cu films at laser fluences of (b) 0.089 J/cm^2 and (c) 0.35 J/cm^2 are shown. The scale bar in the photos corresponds to $1 \mu\text{m}$.

The model indicates that there is another ablation threshold at $F_{th,H} = 0.30 \text{ J/cm}^2$. Therefore, the ablation mechanism is not affected by the thickness of metal in the laser fluence range of interest.

Figure 2 shows the dependence of the periodic structure interspaces on laser fluence. The experimental results indicate that grating structures were formed on copper thin film in the fluence range from 0.08 to 0.64 J/cm^2 . In order to estimate the interspaces of the grating nanostructures, we use the simple method of reading the distance between two neighboring nanostructures, as observed by scanning electron microscopy (SEM). At a laser fluence of 0.089 J/cm^2 , the grating structures had an interspace of 362 nm , which was much shorter than the laser wavelength of 800 nm . For laser fluences greater than 0.127 J/cm^2 , the interspace increased up to about 670 nm as laser fluence increased. The interspaces of copper thin film observed in the present experiment were in good agreement with the interspaces of copper bulk metal reported previously.^{30,31} Figures 2(a) and 2(b) show surface morphologies of Cu thin films after laser pulse irradiation. The grating structures were oriented perpendicular to the laser polarization direction.

Figure 3 shows typical electron diffraction patterns of selected $3 \times 3 \mu\text{m}^2$ areas of Cu thin film. The patterns show that the nonirradiated region had a single-crystalline structure [Fig. 3(a)], whereas the irradiated spot was polycrystalline [Figs. 3(b) and 3(d)] or amorphous in nature [Fig. 3(c)]. In Fig. 3 the diffraction peaks observed at three different laser fluences are also shown. To investigate the degree of crystallinity, the spectral line width of the (220) diffraction peak was analyzed. For high fluences [as shown in Fig. 3(b)], the diffraction peaks of Cu and Cu_2O were observed. The spectral width of the (220) diffraction peak at a fluence of 350 mJ/cm^2 is ~ 1.4 times wider than that of nonirradiated Cu thin film. At medium laser fluence [as shown in Fig. 3(c)] the diffraction pattern shows that the irradiated region consisted of Cu, Cu_2O , and a material with a $3.27\text{-}\text{\AA}$ separation between

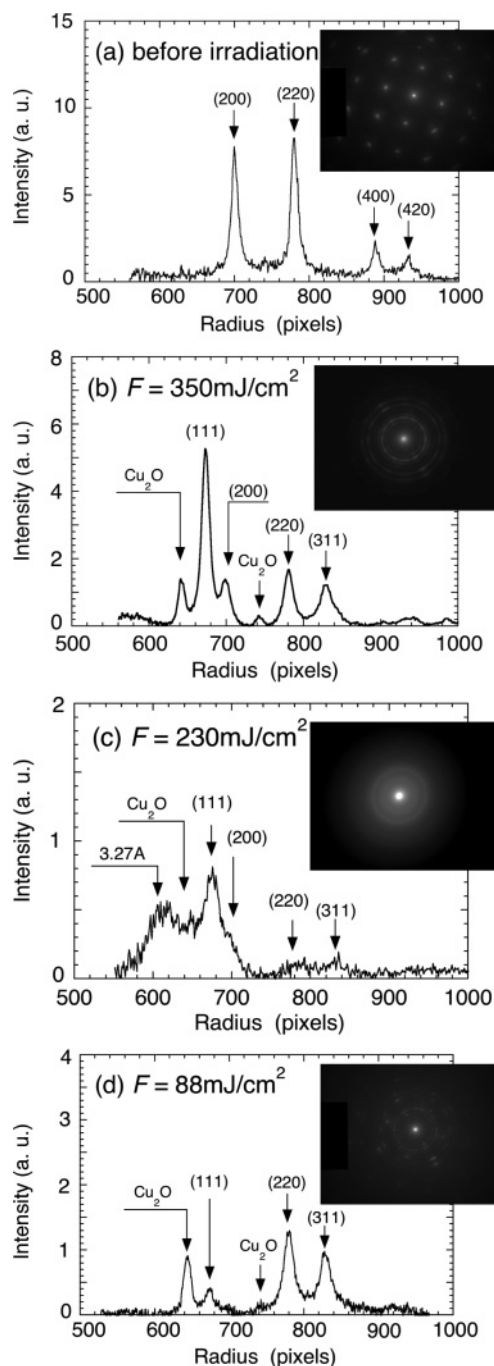


FIG. 3. Electron diffraction patterns of thin Cu films (a) before irradiation, (b) at 0.35 J/cm², (c) at 0.23 J/cm², and (d) at 0.088 J/cm².

atomic planes. At this fluence, the spectral width of the (220) diffraction peak could not be precisely estimated because the diffraction signal was too small. Therefore, the spectral width of the (111) diffraction peak was used to estimate the degree of crystallinity. The spectral width of the (111) diffraction peak at a fluence of 230 mJ/cm² is about threefold wider than that at 350 mJ/cm². Therefore, the irradiated spot was transformed into a partially amorphous state. The material with a 3.27-Å atomic plane separation could not be assigned a structure because its diffraction peak was not matched to hydrogen compounds³⁵ produced in laser ablation.

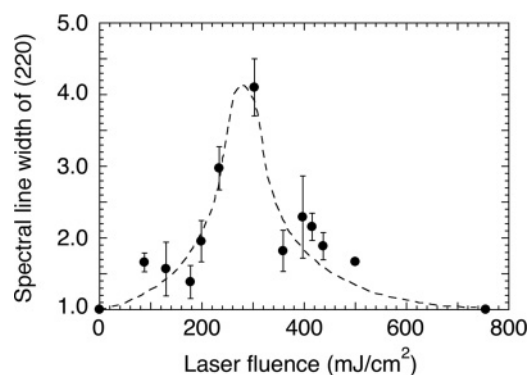


FIG. 4. Dependence of spectral line width of the (220) diffraction peak of a Cu film on laser fluence. The spectral line width is normalized by the width of the (220) diffraction peak before irradiation by a laser pulse. The dotted line is a visual guide.

Figure 4 shows the dependence on laser fluence of the spectral line width of the (220) diffraction peak. The spectral line width is normalized by the width of the (220) diffraction peak of nonirradiated Cu film. The optimum laser condition needed to create the amorphous state in a Cu film was clearly seen to be a fluence of 230–300 mJ/cm².

Many papers have been published on the physics of amorphization of semiconductors^{36–39} and metallic alloys^{40,41} by femtosecond laser annealing and/or ablation. Unfortunately, the physical discussions are mainly limited to the cooling rate and phenomenological viewpoints that consider the laser fluence necessary for amorphization. On the contrary, only a few studies have focused on single-component metals, especially near the ablation threshold in which we are currently interested. Generally, metals have a large nucleation frequency, and consequently very high cooling rates of the order of 10⁶ K/s are required to suppress nucleation. The process of rapid cooling is generally invoked to explain the transformation to an amorphous state in the laser fluence range $F < 10$ J/cm². In such a mechanism, the process of rapid cooling creates the amorphous state before crystallization occurs. The process has been analyzed by molecular dynamics simulations^{36–38} based on the thermal diffusion model. In that model, the amorphous layer thickness is assumed to be characterized by the heat-affected length. There, the heat-affected length was defined as the distance between two points where the temperatures are the boiling point T_b and melting point T_m , respectively. The heat-affected length for Cu (Ref. 2) calculated by simulation increased with increasing laser fluence in the range $F = 0.01$ – 10 J/cm². Our experimental result is quite different from the trend in laser fluence from the calculation. Thus this model is not valid for explaining our data.

The experimental results might suggest that the amorphous Cu thin layer was produced by the Coulomb explosion of Cu ions at the sample surface. The energy distribution of ions emitted from Cu under femtosecond laser ablation has been measured by time-of-flight mass spectrometry in the laser energy fluence range of 0.1 to 1.2 J/cm².³² We briefly describe the results here. Copper ions with peak energy of 30 eV were produced at a low laser fluence of 0.136 J/cm². The energy distribution extended to ~1 keV. The peak ion energy was proportional to the laser energy fluence, $E_{\text{peak}} \propto F^{1.19}$. It is

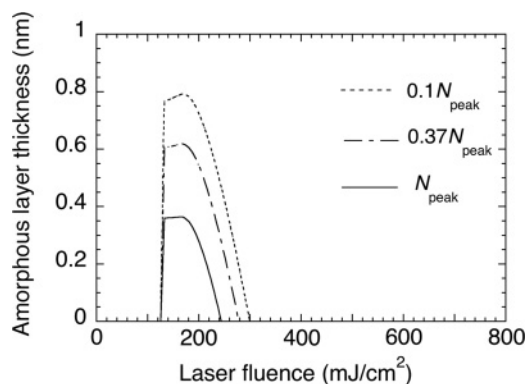


FIG. 5. Dependence of the amorphous thickness layer on laser fluence for three different definitions of the injection depth of Cu ions. The depth of ion injection is estimated by the ion distribution profile from the Monte Carlo program SRIM2010. The effective injection depth of Cu ions was defined from the peak ion concentration N_{peak} by the locations of N_{peak} (the stopping range), $0.37N_{\text{peak}}$ (the $1/e$ level), and $0.1N_{\text{peak}}$ (the 10% level). The thickness of the amorphous layer was estimated by subtracting the ablation depth for one pulse irradiation from the ion injection depth.

possible that high-energy ions can penetrate the metal surface and transform a thin surface layer from a single-crystalline structure to an amorphous structure. The depth of ion penetration is estimated from the ion energy distribution using the Monte Carlo program SRIM2010.^{42,43} In the simulation, 80 000 copper ions with energy E_{peak} were injected into a Cu surface at normal incidence. Cu ions with energy greater than 25 eV are necessary to create the amorphous structure since the displacement energy of the Cu substrate is 25 eV.⁴⁴ Therefore, the contribution of Cu ions with energies less than 25 eV is neglected in the simulation. The simulation results show a peak concentration N_{peak} of injected ions at the stopping range and the ion concentration decreases as the depth of the Cu film increases. The effective injection depth of Cu ions was defined in three ways using the peak ion concentration: by the locations of N_{peak} (the stopping range), $0.37N_{\text{peak}}$ (the $1/e$ level), and $0.1N_{\text{peak}}$ (the 10% level). At the same time, a thin surface layer is ablated according to the ablation rate shown in Fig. 1. Therefore, the amorphous thickness can be deduced by subtracting the ablation depth for one pulse irradiation from the ion injection depth. Figure 5 shows the results of calculations using these considerations. The calculations clearly show the optimum laser fluence for creating amorphous Cu at the peak energy of Cu ions. The experimental result is in relatively good agreement with this estimate, although there is a discrepancy between the laser fluence ranges for the creation of an amorphous state. This discrepancy is considered to arise from the ions' injection to laser-produced plasma. For femtosecond laser-matter interactions, the laser plasma is

already produced on the solid-state matter before the peak of the pulse arrives at the metal surface. Then the femtosecond laser pulse induces the surface-plasma wave at the interface between free space and the laser-produced plasma via the parametric decay process. The plasma wave travels slowly, at less than 10^{-2} times speed of light, and an ion-enriched local area appears. Before the next electron wave peak arrives, the ions experience a strong Coulomb repulsive force and can be exploded. Through this process, periodic grating structures with an amorphous state are formed. Thus the exploded ions can inject into laser-produced plasma on metal surface. The depth of ion penetration is inversely proportional to the density of the material. With the parametric decay model, the density of the produced plasma can be estimated as $1.35 \times 10^{21} \text{ cm}^{-3}$ at the laser fluence of 0.3 J/cm^2 . This density is much lower than the density of the solid state ($= 8.47 \times 10^{22} \text{ cm}^{-3}$) for copper. The density of the plasma is increased as the laser fluence increases. Thus, the effective injection depth for the ions near the fluence of 0.3 J/cm^2 might be deeper than that of the simple ion injection calculated by simulation. This deeper injection depth is attributed to the discrepancy between the laser fluence ranges for the creation of an amorphous state. The experimental observations, therefore, seem to be consistent with the interpretation that the amorphous state is produced by the Coulomb explosion of ions localized on the metal surface by an intense femtosecond laser pulse.

IV. CONCLUSION

In conclusion, the crystal structure of a Cu thin film with a self-organized grating structure induced by femtosecond laser ablation was analyzed using a transmission electron microscope. The laser energy fluence range was $0.08\text{--}0.64 \text{ J/cm}^2$. Grating structures with an amorphous structure were formed in the fluence range from 0.23 to 0.3 J/cm^2 , while grating structures with a polycrystalline structure were produced in the fluence ranges of $F < 0.2 \text{ J/cm}^2$ and $F > 0.35 \text{ J/cm}^2$. A model based on the injection of high-energy ions that were produced by Coulomb explosion on the metal surface could satisfactorily and qualitatively explain the experimental results.

ACKNOWLEDGMENTS

We thank T. Kanaya, K. Nishida, and T. Terashima for their assistance with SEM and atomic force microscope (AFM). This study was financially supported by a Grant-in-Aid for Scientific Research (C)(No. 22560720) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, the Research Foundation of the Murata Science Foundation, and the Amada Foundation for Metal Work Technology, and was partially supported by a Grant-in-Aid for the Global COE Program "The Next Generation of Physics, Spun from Universality and Emergence" from MEXT, Japan.

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